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ESTABLISHING THE REASONS AND TYPE OF THE ENHANCED CORROSION IN THE CRUDE OIL ATMOSPHERIC DISTILLATION UNIT

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Abstract

The aim of the present paper is to establish the reasons for the enhanced corrosion observed in the crude oil atmospheric distillation unit of LUKoil Neftochim Bourgas Co. The results from the investigation define the measures necessary to be taken to reduce the risk of accidents and prove the necessity for preliminary monitoring of the sulfur and naphthenic acids content in the raw material processed. World experience shows that the processing of petroleum with high content of naphthenic acids results in accelerated degradation of equipment in the temperature range 200 - 400°C. Under these conditions characteristic for the middle-distillate fractions of the atmospheric and vacuum installations, naphthenic acids of low molecular weight are produced which are highly active towards metals. To avoid unwanted consequences for the technological equipment, it is necessary to determine the total acidity number (TAN) and naphthenic acids number (NAN), beside the routine analyses. When the presence of naphthenic acids exceeds certain limits then proper combination of measures should be taken to protect the petroleum processing installation against corrosion.

Key Word: Naphthenic acids; high temperature corrosion; corrosion in an atmospheric distillation unit.

1. Introduction

Naphthenic acids are classified as carboxylic mono-acids with general formula R(CH2)nCOOH, where R is some cycloaliphatic structure. A number of authors use the term "naphthenic acids" as reference to all the carboxylic acids present in petroleum. The heavy kinds of petroleum, due to their specific origin, usually have higher content of acids while paraffin petroleum contains smaller number of acids [1,5]. In his paper, Trond Erik Havre characterized the naphthenic acids as the products of biodegradation of hydrocarbons in petroleum. They are biological markers closely related to ripening and the degree of biological degradation in the petroleum fields [1,2].

Marit-Helen Ese and Peter K. Kilpatrick* considered naphthenic acids to be complex mixture of compounds containing 10 to 50 carbon atoms and 1 to 6 saturated rings bonded by short alkyl chain ending with carboxylic group. The distribution of carbon content and number of rings differs among the different kinds of petroleum and the distillate fractions. Naphthenic acids of small TAN and medium molecular weight have quite different structures [1,3]. Figure 1 shows examples of structures of naphthenic acids which might be found in crude oils.

On his presentation „Naphthenic Acid. Corrosion Control Strategies", Randy Rechtien visualized the action mechanism of naphthenic acids based on their physicochemical properties [6]. Generally, naphthenic acids are soluble in hydrocarbon media and only the low molecular weight ones are soluble in water. They are concentrated in the temperature interval of kerosene and diesel fractions and affect primarily the zones of high fluid velocity [5,11].

They react with iron to form iron naphthenate and release atomic hydrogen which diffuses through the metal and remains as molecular hydrogen on its surface [6]:

$$Fe + 2RCOOH \rightarrow Fe(RCOO)_2 + H^0 \quad (1)$$

$$2\,H^0 \rightarrow H_2 \quad (2)$$

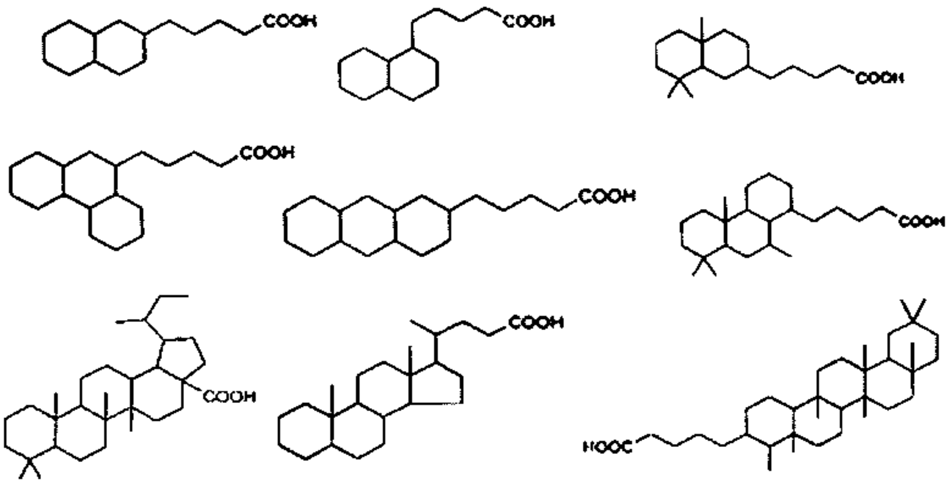

Fig. 1 Examples of structures of naphthenic acids that may be found in crude oils.

Naphthenic corrosion is an aggressive form of local corrosion related to the processing of crude oil with total acidity number higher than 0.5 mgKOH/g. The typical naphthenic corrosion is observed in the temperature interval 200 – 400°C. According to the expert opinion of S. Vrijhoeven in the Nalco report, corrosion rate increases thrice per each 55°C increase of temperature in this interval [4]. Vrijhoeven suggested that the attack is usually limited within the zones where the condensing acids could contact with metal surface (e.g. lower part of the plates), i.e. where the protective layer of hydrocarbons diluting the acids is missing [4].

2. Approach and experimental procedure

The aim of the present study is to establish the reasons for a real accident observed in the installation for atmospheric distillation of petroleum of LUKoil Neftochim Bourgas Co. and taking precaution measures to prevent such accidents in future.

By the end of March 2007, during planned maintenance of the installation for atmospheric distillation 4, some plates of the rectification column (between 6^{th} and 12^{th}) were found sunk. The rectification column is manufactured from bimetal with basic material – low alloyed steel 16GS and the cladding – steel 0X13. Metal identification analyses carried out showed that the binding elements – plates, bolts, nuts, etc. have been made of steels 1X13, 2X13 and X18N9T while the main beams were made of carbon steel St3. According to literary data, steels 0X13, 1X13 and 2X13 are stable in media of average aggressiveness containing small amounts of hydrochloric acid and hydrogen sulfide at temperatures up to 500°C. Steel X18N9T is reported to be stable in oxidative, acidic and alkali media[9] .

After thorough examination of the corroded equipment, the metal surface of the main beams was found to be highly corroded with deep pits, at some places even perforated[9]. The type of corrosion pattern is quite specific, resembling lace. Relating the type of corrosion with the temperature interval where it had occurred and taking into account some literary reports [4,5], it could be suggested that it had been caused by the presence of naphthenic acids. The results obtained from the visual examination were confirmed by the microscope analysis carried out by Nalco Co.

The metal sample shown in Fig.2 is part of a beam mounted at the inlet of the rectification column, subjected to temperatures up to 360°C. The sample surface is covered with spots and pits of oval shape, with perforations at some places. The average beam thickness was measured to be 4.6 mm, compared to the initial thickness of 6.0 mm. All surfaces were covered with fine black sulfide layer [4].

Fig. 2 A part of plate on the tray section

Fig. 3 Binding elements – plates, bolts and nuts on the tray section

Figure 3 shows the binding elements to the same beam, made of high alloyed kinds of steel. The photograph clearly shows that the corrosion affected only the beam [9].

The microscope analyses of part of the beam (Fig.4) showed that the metal microstructure contained metal carbides and manganese sulfide precipitated in the ferrite mixture [4]. Metal surface covered with fine layer of iron corrosion products, mainly FeS [4], is presented in Fig. 5.

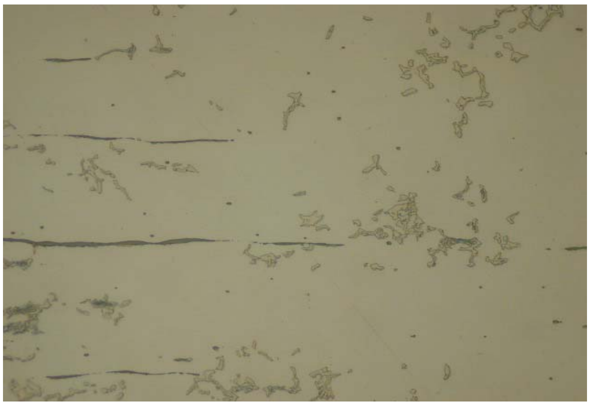

Fig. 4 Metal microstructure consisting of iron carbides and elongated manganese sulfide precipitates in a matrix of ferrite

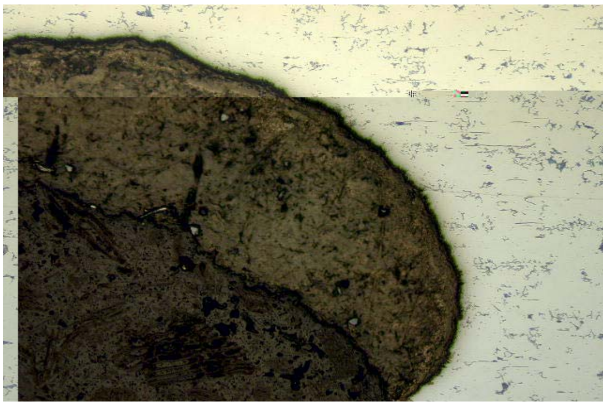

Fig. 5 Rounded depression profile that is lined by a thin corrosion product layer

It is well known that iron sulfide exerts certain protective effect against naphthenic acids. In this respect, some researchers stated [15,16] that petroleum with high TAN values and sulfur content u to 2-3% has lower corrosion activity compared to petroleum with lower TAN values and lower sulfur content. The reason for this is the lack of sulfur necessary for the formation of protective FeS layer so the naphthenic acids attack directly the unprotected metal surface.

3. Results and discussions

Despite the undisputable proofs for the presence of naphthenic corrosion, a comparison of the petroleum properties for this period was carried out to exclude the probability for effects of other corrosion-active components (Table 1)*.

In the period investigated, there were no significant divergences in the properties of the Russian export mixture for the individual tanker samples. Generally, it can be concluded that the values comply with the certified ones.

Table 1 Average surveyor properties of petroleum from October 2006 to April 2007.

Crude data	Test method	Date						
		10.06	11.06	12.06	01.07	02.07	03.07	04.07
1. Density at 20°C,g /cm, API	EN ISO 3675	0,8670 31,07	0,8639 31,65	0,8653 31,39	0,8677 30,94	0,8661 31,24	0,8649 31,46	0,8644 31,55
2. Sulfur, %	ASTM-E 443	1,39	1,31	1,16	1,30	1,40	1,31	1,22
3. Water, %	ASTM-D 4006	0,020	trace	trace	trace	0,15	0,15	0,25
4. Salt, mg/l	BDS 5502	6	6	12	5	11	13	10
5. Sediments, %	ST на SIV 2876	0,0062	0,0061	0,0086	0,0069	0,0054	0,0066	0,0062

** The average surveyor testing of petroleum were performed by the independent arbitrary laboratory „Saybolt"*

Table 2 General properties of Russian export mixture (REBCO) – certified according to GOST TU 39-1623-93:

Density at 30°C g /cm^3	API	Sulfur, %	Salt, mg/l	Water and sediments, max %
0,870	32	1,8	100	1,2

The next step in the investigation was the check the content of chlorides at the inlet of the atmospheric distillation installation, after desalination and by the processes of rectification.

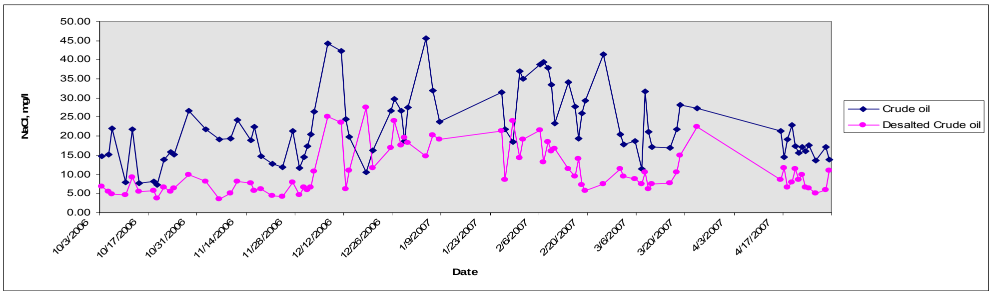

Fig. 1 Content of chlorides at the inlet of atmospheric distillation 4 and after the electric dehydrators for the period October 2006 – April 2007

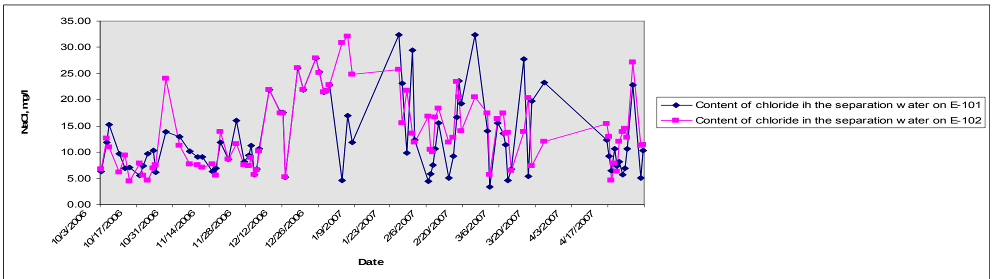

Fig. 2 Content of chlorides in separation waters after benzene removing and rectification columns for the period October 2006 – April 2007

As can be seen from Figs. 1 and 2, there were some individual high values of chlorides content, e.g. after the electric dehydrators and after the columns which are probably due to erroneous sample taking or ineffective performance of the electric dehydrators. The increased chlorides content after the rectification column, compared to the initial petroleum composition, clearly indicated for the presence of organically bonded chlorides in petroleum and their probable decomposition in the oven. According to H. Shalaby, the organic chlorides are not removed after desalination and they tend to decompose under high temperature to form HCl which, in turn, reduces the pH values and initiate accelerated corrosion in the up most sections of the distillation installation and the condenser unit [12]. It should be noted here that this kind of corrosion is totally different from the one induced by the high content of naphthenic acids.

The laboratory testing of the separation waters after benzene removing and rectification columns in the period October 2006 – April 2007 did not show deviations in pH values and presence of soluble iron. This is due to the efficient performance of the inhibitor system implemented for protection of the equipment in these units. This aim of this protection is to block out the corrosion processes initiated by the presence of salts and sulfur containing components in the flow. It consists of neutralizing and film-forming inhibitors [17,18]. Unfortunately, these types of inhibitors do not have protecting effect against the naphthenic acids.

Since only petroleum of Russian origin has been processed for the recent years, the total acidity number (TAN) has not been measured for this period. After the accident, the TAN of the petroleum supplied and the distillate fractions obtained were determined according to ASTM D 664 – 95 [13] and ASTM D 3242 -01 [14].

Table 3 Total acidity number of an average petroleum sample and distillate fractions in March (analyses of the Research Laboratory of LUKoil Neftochim Bourgas Co):

Middle test - March	TAN, mg KOH/g	Test method
Crude oil	0,56	ASTM D 664 - 95
TBP cut point:		
C5 - 110ºC	0,018	
110 - 180ºC	0,067	ASTM D 3242 -01
180 - 240ºC	0,179	
240 - 360ºC	0,287	

The values of TAN for petroleum supplied in March 2007 were above the limit of 0,5 mgKOH/g [11,15], - a value above which the petroleum is considered to be acidic and special measures should be taken before its processing.

In the course of the events during this period, at the beginning of April 2007 the performance of the atmospheric distillation installation 4 had to interrupted emergently due to a problem with the oven before the rectification column. Immediate examination showed that the serpentine in third convection section was punctured. The reason for this was found to be changed material – the serpentine was made from carbon steel St20 instead of the thermally resistant steel 15X5M. Ultrasonic measurements showed that the serpentine wall thickness observed (1,6 – 2,2 mm) [10] was much smaller then the designed one (8 mm). As it has been reported [7,8] for similar ovens and technological conditions – petroleum temperature at the inlet 240°C, temperature at radiant chamber outlet about 860°C, temperature at the convection chamber outlet about 350-400°C – the use of carbon steels St10 and St20 is allowed only for the tubing in the convection part, i.e. where the temperature is below 400°C.

Back in 1874 Suhotin et al. published their thorough investigation on this problem. The choice of the construction materials for the processing of petroleum with high sulfur content and naphthenic acids is crucial, as can be seen from the data presented in Table 4 [5].

The steel samples were tested at sulfur content in petroleum 1.2% and total acidity number 0.4 – 0.5 mgKOH/mg, i.e. properties similar to those of the export mixture of Russian origin processed. According to Suhotin et al., the depth of corrosion penetration in St.3 for 42 days in the rectification column was 6.1 mm/y which undoubtedly indicated for accelerated corrosion of carbon and low alloyed steel grades under increased content of naphthenic acids and the technological conditions employed [5]. The damage observed in the LUKoil Neftochim Bourgas Co., mainly on the beams supporting the plates in the zone of petroleum inflow into the column were caused for about the same period of time which also sustains the opinion that severe naphthenic corrosion had taken place.

Table 4 Corrosion rate of different grades of steel under service testing of an installation for atmospheric distillation of petroleum:

№	Sample exposition	Steel grade	Petroleum		Corrosion rate, mm/y
			Acidity, mg KOH/ml	Sulfur content, %	
1.	Oven tubes	Carbon steel	320-380	1,2	5,75
2.	Petroleum transfer line of atmospheric column	Carbon steel			
3.	Rectification column (tests duration 1000 h)	St3 X5M 0X13 X18N10T			6,1 2,6 0,86 0,017

4. Conclusions

In conclusion, we can summarize the well known practical measures of utmost importance which should be taken to protect the technological equipment from naphthenic corrosion used in refineries processing crude oil with high content of naphthenic acids: proper management of the petroleum supplies, definition of the critical factors and assessment of the risk in its processing, reasonable blending of the different batches, choice of suitable material for the equipment, chemical inhibition, continuous monitoring and automated corrosion control, optimization of the corrosion management programs.

The critical factors of crude oil which must be controlled are these indicating its corrosion aggressiveness: density, content of water soluble salts, total sulfur content, organically bonded chlorine, total acidity number (TAN), naphthenic acids content (NAN), contents of metals – Ni, V, Fe, Hg, Se, etc. The corrosion effect of the naphthenic acids can be diminished by blending petroleum of high neutralization number with one of lower neutralization number to obtain raw material with acidity number not higher than 0,5 mgKOH/g. The choice of suitable construction material means the use of corrosion-resistant steel like austenite stainless steel grades – chromium-nickel-molybdenum alloyed ones which have excellent resistance to raw materials containing hydrogen sulfide, chlorides, organic and inorganic acids under high temperature. The report of Nalco Co. stated that steels of grade 316SS or 317SS with molybdenum content above 3% are the most suitable for manufacturing of the technological equipment working under these conditions. The introduction of automated corrosion monitoring would also allow the optimization of the amount of inhibitors introduced to change the medium characteristics or technological parameters. The methods of corrosion control in the presence of naphthenic acids are simply determination of metal loss using corrosion coupons, ultrasonic or hydrogen infiltration measurement of the thicknesses of equipment walls.

Obviously, when supplying petroleum with high content of naphthenic acids, it is necessary to take all precaution measures before letting it into the installation. The processing method should be carefully selected to avoid hazardous situations and rapid deterioration of the technological equipment at certain points of the installation for atmospheric distillation of petroleum.

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